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The wavelength modulation spectrum of ion-implanted silicon

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The radiation damage and its subsequent annealing in phosphorus implanted Si are studied by wavelength modulation spectroscopy. The distinct structure at $\lambda = 360$ nm of the wavelength-derivative spectrum is implemented as a parameter to specify the damage level in Si crystals. This characteristic peak completely fades away when the implanted dose exceeds 3×10^{15} ions cm^{-2} . Isochronal and isothermal annealing indicate that the removal of vacancy-like defects starts at rather low temperatures ($\sim 200^\circ\text{C}$) while the recrystallization of the disordered layer starts at a temperature near 500°C . Sheet resistance of the samples measured by a four-point probe has been found to be closely related to the wavelength modulation spectrum.

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Ion implantation has been used as an alternative of thermal diffusion for more accurate control of doping concentration and doping depth. The disadvantage of ion implantation is the introduction of radiation damage. Several experimental techniques such as EPR¹ and infrared² measurements had been used to identify the nature of the major defects. Rutherford backscattering is a convenient method to determine damage level and depth.^{3,4} Electron microscopy and positron-annihilation lifetime measurements⁵ have also been used to study the ion damage effect. Considering the well-known relationship between optical reflectivity and electronic band structure of solids,⁶ one may expect a close connection between radiation damage and optical spectra. For crystalline Si, characteristic lines appear near the critical points of the joint density of states. The modulation spectroscopy^{7,8} revealed that the intensity of the characteristic lines

of a mechanically polished sample was enhanced after chemical etching. The spectrum of amorphous silicon^{9,10} even showed a total smearing out of the characteristic lines. All these experiments suggested the possibility of probing the defects on the surface of solids by means of a modulation spectroscopy. However, only few experiments have been reported up to now.¹¹

The projected depth of implanted ions depends on the energy and mass of incident ions, the target material, and the surface orientation. The defect clusters expand their domains as the implanted dose increases, and finally a continuous random structure called amorphous layer is formed. In this work, the variations of the reflectivity and wavelength derivative spectrum at various implanted doses and annealing conditions were measured by using a double-beam single-detector wavelength modulating spectrometer.^{12,13} This system can effectively eliminate the strong characteristic lines of the Xe arc light source and gives the true absolute

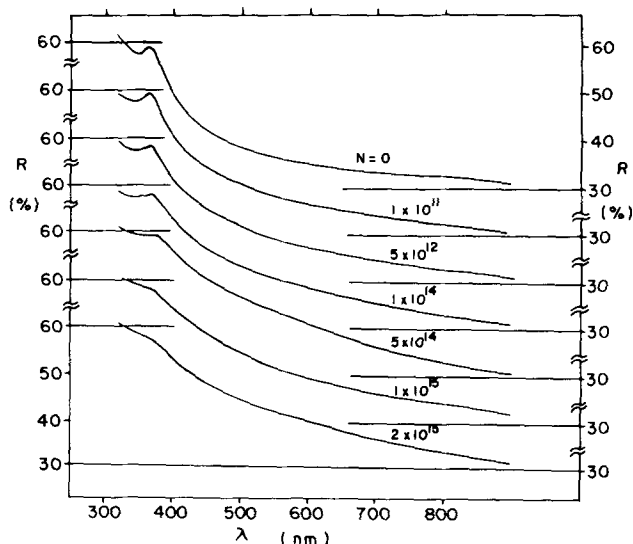


FIG. 1. The absolute optical reflectivity of phosphorus-implanted silicon.

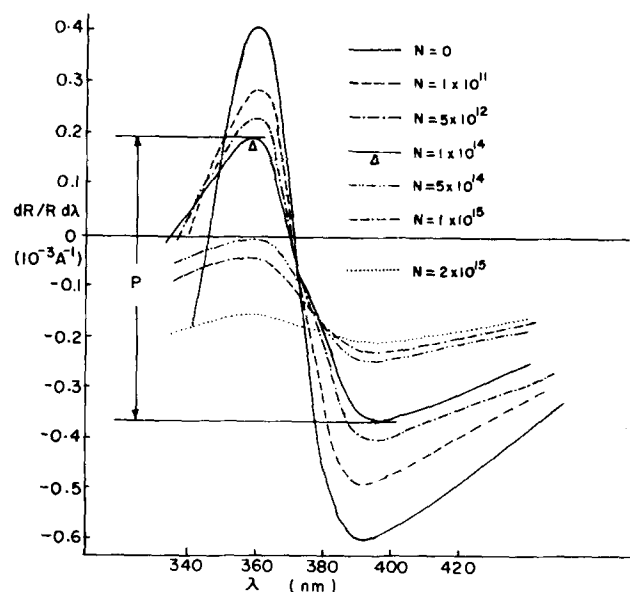


FIG. 2. The wavelength-modulated spectrum of the implanted samples near the 3.4 eV critical point of crystalline silicon.

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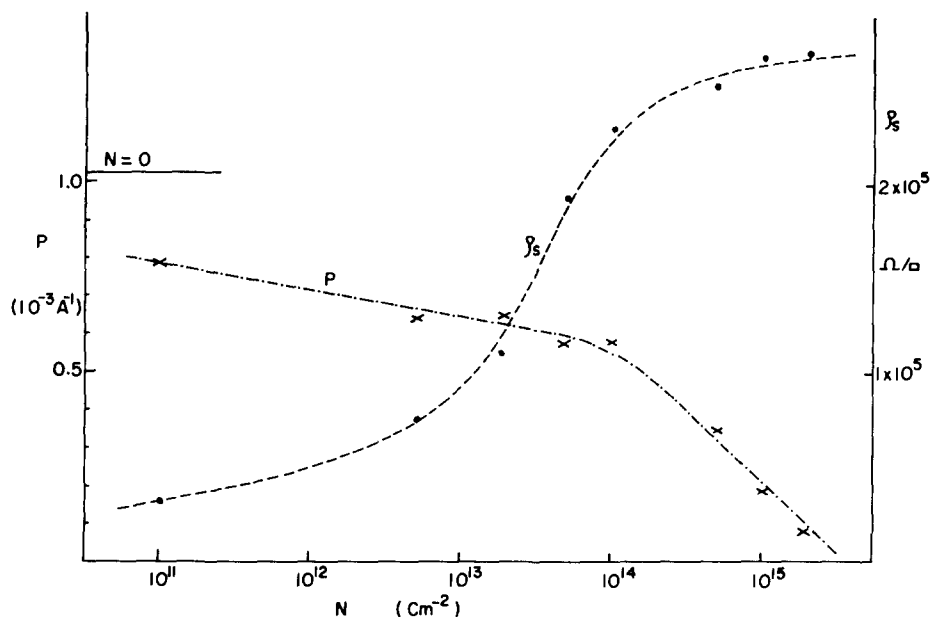


FIG. 3. The plot of parameter P and sheet resistance ρ_s vs implanted P^+ doses.

reflectance. The [111]-oriented p -type silicon wafers with a resistivity ρ of $2\ \Omega\ \text{cm}$ were implanted at room temperature by phosphorus ions at a beam energy of 150 keV with doses ranging from 1×10^{11} to 2×10^{15} ions cm^{-2} . As can be seen from the absolute reflectivity as shown in Fig. 1, the flat part of the spectrum does not change even when the implanted dose is increased up to 2×10^{15} ions cm^{-2} . The characteristic band transition $L_3 \rightarrow L_4$ near 3.4 eV ($\lambda \approx 360\ \text{nm}$),⁸ however, is smeared out due to Gaussian broadening by radiation defects which act as random scattering centers. Since the projected range of P^+ ion¹⁴ ($\sim 2000\ \text{\AA}$) is less than the optical penetration depth ($\sim 1\ \mu\text{m}$) in the visible and ultraviolet range, the variation of the spectrum truly reflects the effect due to ion implantation.

Figure 2 shows the derivatives of the wavelength modulation spectra near the critical point indicating that the line shapes depend greatly on the implanted doses. It is convenient to define the peak to peak value of this structure,

$P = dR/Rd\lambda|_{p-p}$, as a parameter to specify the degree of perfection of the crystal. With this definition, a direct comparison between the results of optical measurement and the sheet resistance, ρ_s , as measured by a four-point probe, is possible. As can be seen from Fig. 3, a general agreement exists between the changes in P and ρ_s as function of P^+ ion fluence. As expected, ρ_s increases and P decreases with increasing P^+ ion fluence. The rate of change, however, does depend on the fluence range. For a fluence up to 1×10^{14} ions cm^{-2} , ρ_s is seen to increase rather rapidly, whereas P decreases more slowly indicating that sheet resistance is strongly affected by the introduction of interstitial atoms, and the carrier mobility drops sharply just before the lattice becomes disordered. For fluences above 1×10^{14} ions cm^{-2} , the effect is opposite; ρ_s is seen to saturate whereas P decreases rapidly. This is a manifestation of the fact that optical spectrum is the major effect of covalence bond structure. The characteristic line will diminish only when the dose is

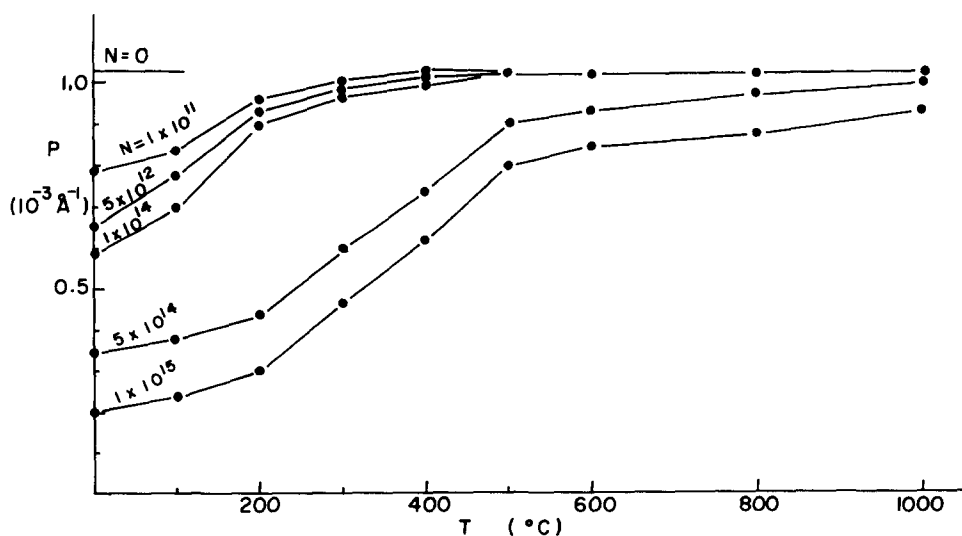


FIG. 4. The plot of P for five-minute isochronal annealing of P^+ implanted silicon at various fluence from 10^{11} to 10^{15} ions cm^{-2} .

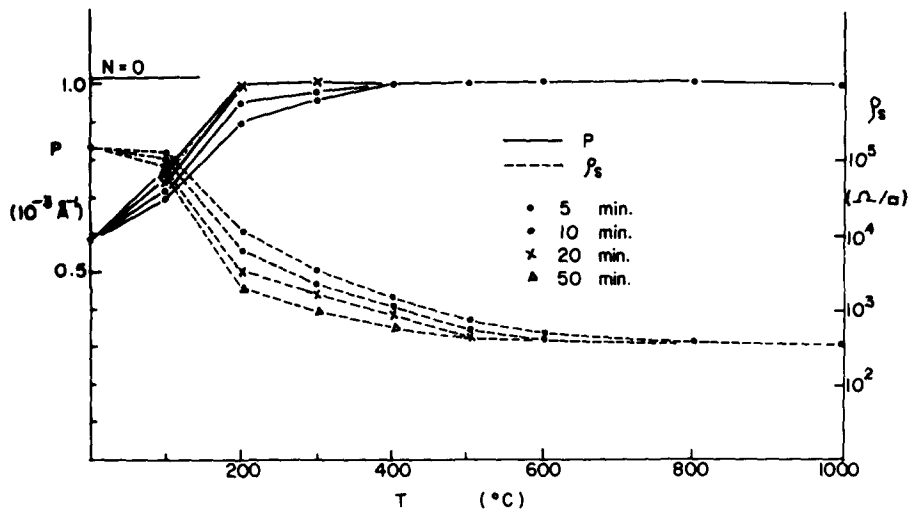


FIG. 5. The plot of P and ρ_s for isochronal annealing of P^+ implanted silicon at fluence 1×10^{14} ions cm^{-2} .

high enough to cause a continuous spreading of defect clusters up to the surface. The transition of defect clusters from isolated to continuous spreading at a fluence of 1×10^{14} ions cm^{-2} had also been verified by the EPR experiment which showed the conversion of isolated-vacancy centers into the amorphous state centers. If the parameter P is assumed to be zero for a completely amorphous structure which occurs at a dose of 5×10^{15} ions cm^{-2} , the fraction of dangling bonds due to ion damages can be written as $S = (N/5 \times 10^{15})^{1/3}$ for an implanted dose of N . Figure 3 clearly shows that P is roughly proportional to $(1 - S)^2$ in the region of highly implanted doses.

The annealing behavior of the implanted samples was observed for the high and low dose ranges. Figure 4 shows the isochronal annealing data by heating the samples in dry nitrogen for 5 minutes at various temperatures. For lightly doped ($< 1 \times 10^{13}$ ions cm^{-2}) samples, the recovery of the parameter P is found to start near 200°C . It indicates that the vacancy-like centers begin to anneal at rather low temperatures. This is in agreement with the result reported by Stein *et al.*² on the annealing of divacancies by using IR absorption measurement.

However, a temperature as high as 500°C is required for significant annealing of the heavily implanted ($> 5 \times 10^{14}$ ions cm^{-2}) samples. This temperature agrees with that observed by Davis *et al.*¹⁵ in backscattering experiments for the annealing of heavily implanted amorphous layers on silicon wafers. It is also fairly close to the temperature observed by Brodsky *et al.*¹⁶ for the recrystallization of the sputtered amorphous-silicon film.

A comprehensive comparison between wavelength modulation spectra and sheet resistance measurements with respect to annealing conditions was carried out. Figures 5 and 6 are the results for isochronal annealing of phosphorus ion-implanted Si at doses of 10^{14} and 10^{15} ions cm^{-2} , respectively. It can be noted that the sheet resistance of the implanted samples recover to its crystalline value at temperatures higher than those needed for the recovery of the parameter P . This is due to the fact that the activation energy E_a for the formation of substitutional dopants is usually higher than the energy E_0 (~ 1 eV) required for the diffusion of a vacancy. In general, $E_a = E_0 + E_p \approx 3$ eV, where E_p is the potential barrier for an interstitial impurity to migrate into the vacant lattice site. This means that the activation of dopants

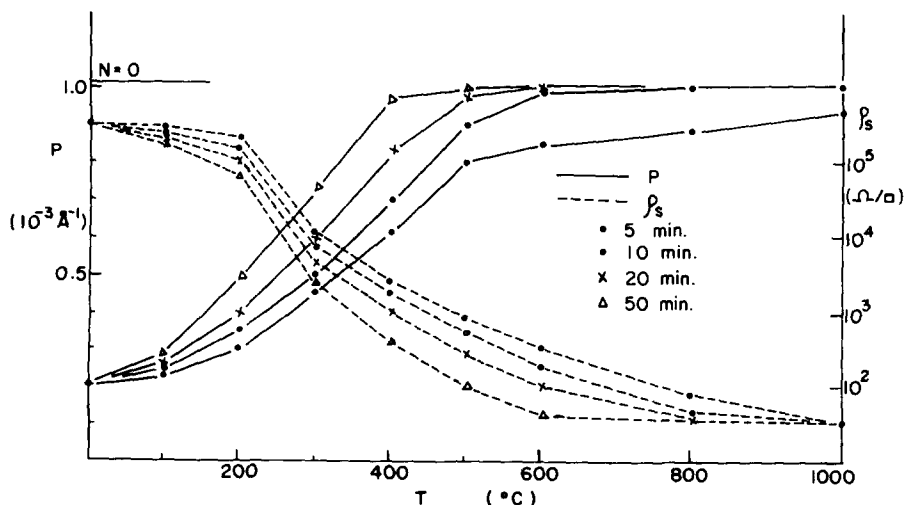


FIG. 6. The plot of P and ρ_s for isochronal annealing of P^+ implanted silicon at fluence 1×10^{15} ions cm^{-2} .

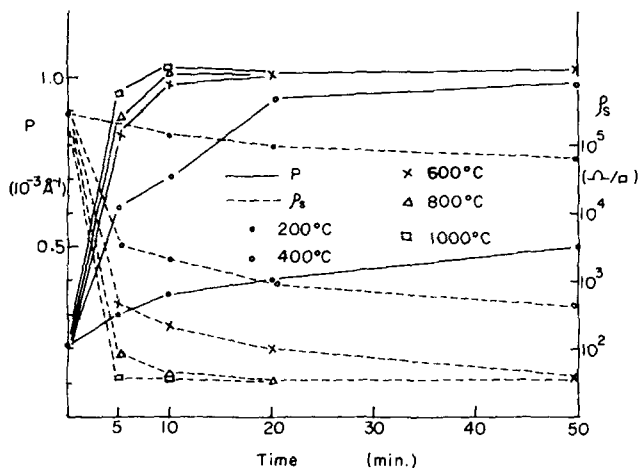


FIG. 7. The plot of P and ρ_s for isothermal annealing of P^+ implanted silicon at fluence 1×10^{15} ions cm^{-2} .

is incomplete even when the implanted layer is fully epitaxially regrown from damage. Figure 7 is a plot of the isothermal annealing of a heavily doped (1×10^{15} ions cm^{-2}) wafer. It shows that significant annealing starts when the temperature reaches 600 °C.

In conclusion, wavelength modulation spectroscopy can be used as a probe to detect the defect levels in semiconductors. As demonstrated in this experiment, the parameter P is roughly proportional to $(1 - S)^2$ where S is the fraction of dangling bonds which is proportional to implanted doses. The measuring technique is simple but is of relatively high

sensitivity. Although this method does not provide specific information on the nature of the defect, it can be useful in the study of surface damages when cooperated with other techniques.

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